

## OCEAN ABYSSAL CARBON EXPERIMENTS AT 0.7 AND 4 KM DEPTH

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### ABSTRACT

Observations from small-scale (20 to 90 litres) CO<sub>2</sub> experiments conducted off the coast of California at 684 m depth and at 3942 m depth are discussed. In both experiments, when the seawater velocity was sufficiently strong, parcels of liquid CO<sub>2</sub> were torn off and transported away as discrete units by the turbulent water current. In the deep experiment, newly formed frazil hydrate was observed at the interface, occasionally including sediment particles. Hydrate furthermore collected and created a floating consolidated solid ("ice") in the downstream end of the trough, dissolving slowly from one day to the next. These observations have important implications for understanding and modelling of larger scale disposal at the seafloor. In particular, when CO<sub>2</sub> is released by the interfacial instability mechanism driven by strong currents, the seawater density increase due to dissolution of CO<sub>2</sub> may not have time to act and stabilize the water column before the discrete parcels of liquid phase CO<sub>2</sub> are advected away from the disposal site. The floating solid that formed at the interface is hypothesized to consist of hydrate and additional trapped seawater. Its appearance was not expected in advance and its role in delaying dissolution can not be determined from the present experimental set-up. A capability for long-term seafloor perturbation experiments is deemed to be crucial both for direct ocean-storage research and for studying effects of invasion of anthropogenic CO<sub>2</sub> from the atmosphere.

### INTRODUCTION

A team of researchers from Japan, USA and Norway have been working together since 2002 within the framework of the Ocean Abyssal Carbon Experiment (OACE) project. The project runs for a three year period until 2005 and includes high-pressure laboratory work, instrument development and theoretical and numerical modelling in addition to field experiments. The fundamental research theme of the project is to carry out novel and challenging experiments to determine the fate of carbon dioxide disposed of on the ocean floor.

The first OACE experiment was performed at 684 m depth in Monterey Bay during the period from 20 to 24 February 2003 using the R/V Point Lobos and the ROV Ventana of the Monterey Bay Aquarium Research Institute (MBARI). In this relatively shallow experiment, buoyant liquid CO<sub>2</sub> was placed in an inverted box 1.2 m above the seafloor. Currents of order 10 to 40 cm sec<sup>-1</sup> occurred, creating eddying motions inside the box. The hydrate covered CO<sub>2</sub>-seawater interface became strongly distorted and apparently posed no significant barrier to dissolution. The layer of CO<sub>2</sub> was completely dissolved within about two days. A pH record obtained approximately 10 cm from the CO<sub>2</sub> showed spikes of low pH down to almost 2 pH units below ambient levels, while insignificant perturbations were recorded immediately below near the seafloor and 2 m downstream. [1] describes this experiment in some detail and discuss the issues and challenges for further experimentation.

The second experiment was performed at 3942 m off San Francisco between 24 and 28 October 2003 using the R/V Western Flyer and the ROV Tiburon. In this deep experiment, a layer of dense CO<sub>2</sub> placed in a rectangular box on the seafloor was exposed to a series of different current speeds controlled by a thruster and to waves generated by a mechanical wave-maker. The response of the hydrate-covered interface was recorded on videotape. An array of pH probes and other sensors provided additional data from the near field. The outflow plume with dissolved CO<sub>2</sub> was sensed with a set of three recording units, each having three pH electrodes and a conductivity-temperature-

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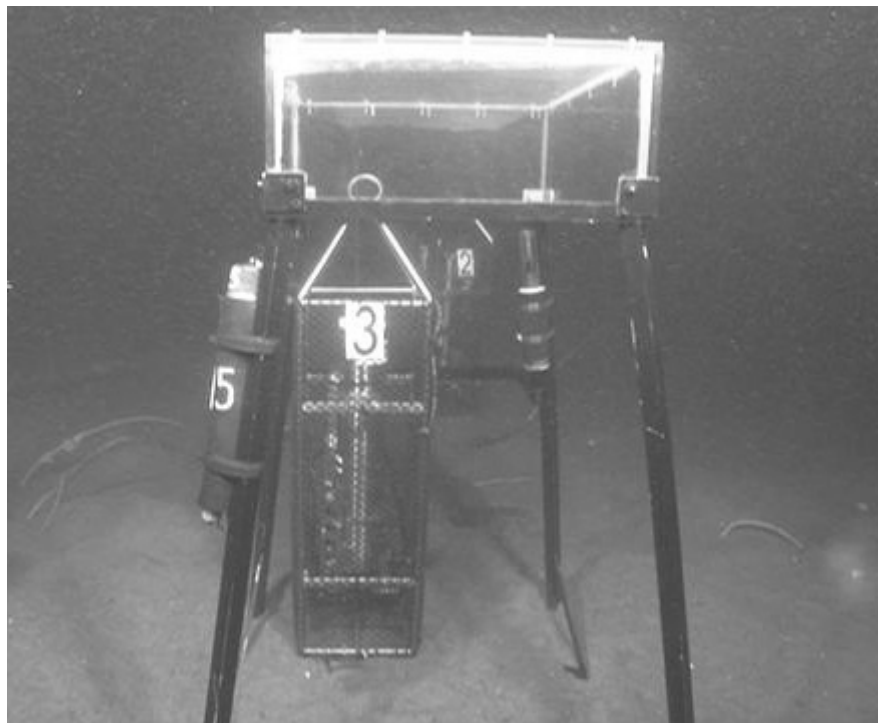
depth-measuring (CDT) device. The units were placed about 50 cm, 1 m, and 5 m distant from the CO<sub>2</sub> source. The experimental set-up is described in [2], while [3] gives further interpretation of the pH records from the outflowing plume. These references also describe a separate CO<sub>2</sub>-kinetics experiment and the use of conductivity sensors as supplements to pH sensors for detection of elevated carbon concentrations. [4] contains an analysis of the fluid dynamics and interfacial wave properties from the trough experiment both in dynamically stable and unstable conditions, and compares the unstable case to theoretical models of Kelvin-Helmholtz instability, while [5] shows further details of the interfacial dynamics.

Common to both experiments was the use of dye injection to visualize the flow field. The first experiment was performed at shallower depth. It also served as a test for procedures and protocols and allowed all groups of the international project team to get acquainted with possibilities and constraints of deep-sea, ROV-assisted experimentation. Naturally occurring currents were strong at the selected time and location and almost unidirectional along the main axis of the inverted box. While these favourable conditions were not fully predictable in advance, they motivated the development of a controllable thruster and wave-maker for use in the second deep-sea experiment. A series of perturbation experiments were then performed at greater depth where CO<sub>2</sub> is negatively buoyant.

The present paper reviews and compares observations from the two experiments performed in 2003. The main focus is on the way in which CO<sub>2</sub> behaves and is transported away from the site in realistic deep-sea conditions where hydrates form and where CO<sub>2</sub> is exposed to sediments. The synthesis of observations is then used as a basis for discussing and presenting best estimates of the fate of larger quantities of CO<sub>2</sub> placed on the seafloor. Plans for the third OACE experiment scheduled for November 2004 and perspectives for larger scale, longer term experiments are briefly reviewed in the discussion section.

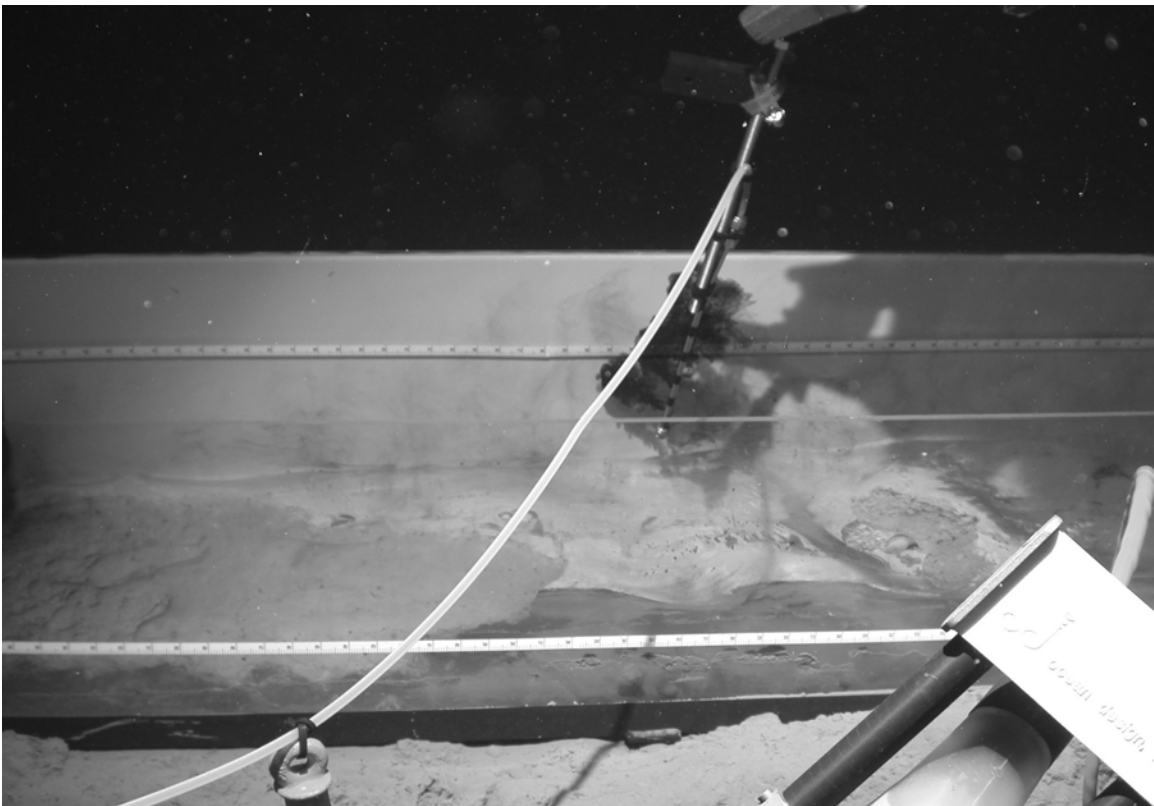
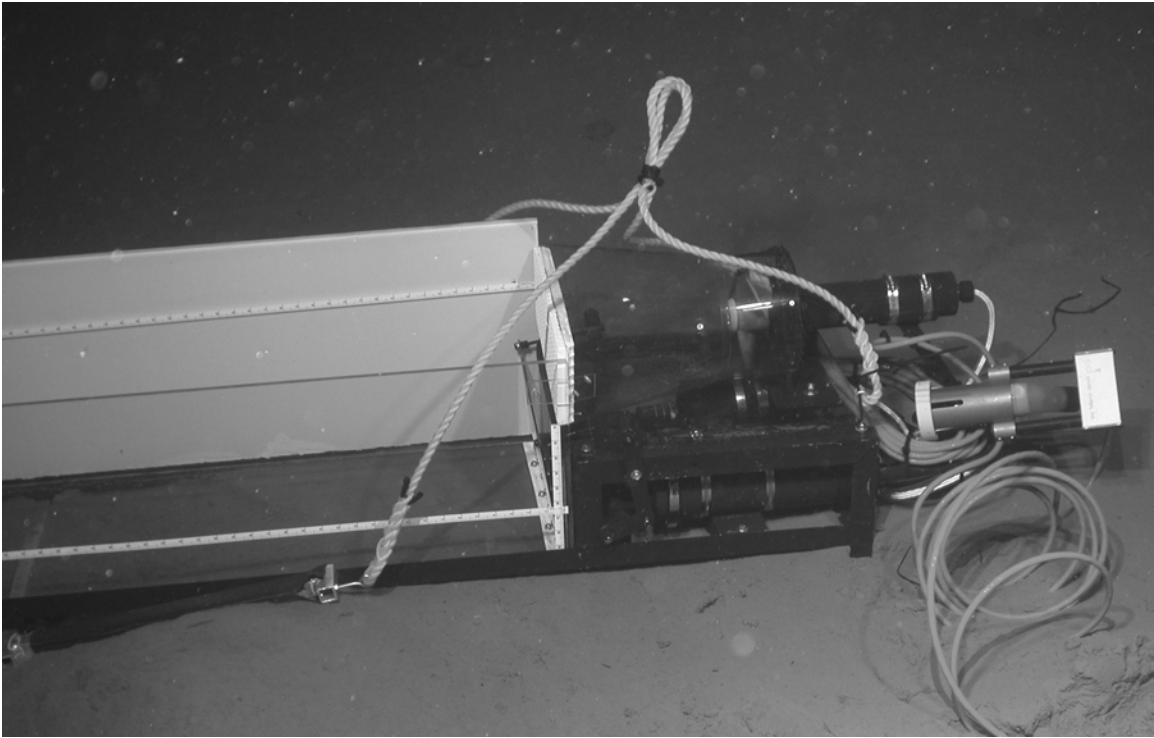
## OBSERVATIONS

The configuration of the first experiment is shown in Figure 1.



**Figure 1:** The inverted trough placed on the ocean floor at 684 m depth; pH probes are located in the cage underneath the trough and on the ocean floor downstream in the natural current direction.

The configuration of the second experiment is shown in Figure 2a, b, and c.





**Figure 2:** a) Upstream end of the trough when placed on the ocean floor at 3942 m; the thruster that produces controlled water flow can be seen at the upper right, with the mechanical wave-maker below it working directly on the endwall of the trough; b) using dye to visualize the water motion in a case with wave perturbation of the CO<sub>2</sub>-seawater interface; some sediment and the floating "ice" can be seen in addition to the wave pattern; c) focus on the consolidated solid downstream.

The ROVs were used for arranging the experimental set-up including stationary pH probes and current meters, for injecting CO<sub>2</sub> and dye and for making high-precision CTD and pH measurements in the near field.

In the first experiment, 20 litres of CO<sub>2</sub> were brought to the ocean floor of which a total of 18 litres were injected into the trough which had a surface area of 0.21 m<sup>2</sup> exposed to flow. Water velocities up to 40 cm sec<sup>-1</sup> were recorded outside the box. Strong motions of the CO<sub>2</sub> surface were induced by the water flow. Eddies formed in the box at almost all times.

In the second experiment, power to the thruster and wave-maker was supplied from the ROV through an underwater connector (Fig. 2a). Ninety litres of CO<sub>2</sub> were brought to the ocean floor, of which about 80 litres were filled into the trough. A series of experiments were then run with different wave-maker frequencies (0.1 to 2 Hz) and different thruster speeds (water currents up to 0.6 m sec<sup>-1</sup>). The trough for CO<sub>2</sub> is 150 cm long, 40 cm wide and 25 cm deep. A movable pH sensor was used to survey the water immediately above the CO<sub>2</sub>-seawater interface. No pH reduction could be registered even when measuring within 2 mm of the interface. The sheared system became unstable with violent turbulent motions when the water current exceeded 18 cm sec<sup>-1</sup>. CO<sub>2</sub> parcels with dimensions in the order of 1 cm and variously shaped were then torn off from the interface moving with the current, eventually over-spilling the downstream end of the trough.

## DISCUSSION

In both experiments, CO<sub>2</sub> was successfully injected into the designated trough, and appeared as a continuous phase at the start of the experiments. Thus, initially there was only a thin layer of hydrate at the smooth interface between CO<sub>2</sub> and seawater. The current speeds were similar in both experiments. If there was any tendency for CO<sub>2</sub> hydrate to consolidate at the interface in the shallow experiment, the hydrate-affected layer remained thin. It is generally believed that all CO<sub>2</sub> that dissolves has to go through an intermediate stage of hydrate. Since this hydrate is more dense than the CO<sub>2</sub>, it was not expected to accumulate to any significant thickness in this experiment, but would, rather, sink into the water below. Upon dissolution, the water becomes more dense and would tend to move away from the interface in the shallow experiment creating compensating vertical currents in the upward direction. Thus the interface will continuously be exposed to water with low concentration, stimulating further dissolution. In the present case, naturally occurring horizontal currents were strong enough to create violent eddies inside the box. Currents are known to reduce the thickness of a diffusion-controlled boundary layer and increase the dissolution rate [6]. A dissolution rate of 3 μmol cm<sup>-2</sup> sec<sup>-1</sup> was experimentally determined from shrinkage of droplets at similar conditions [7]. This corresponds to more than 10 cm day<sup>-1</sup>, so as expected, all the CO<sub>2</sub> was dissolved during the two day duration of the shallow experiment.

Also in the deep experiment, pure CO<sub>2</sub> hydrate is more dense than liquid CO<sub>2</sub>. Thus, hydrate would tend to sink into the liquid CO<sub>2</sub> if it becomes thick enough to overcome the interfacial tension. Such sinking does not, however, seem to occur in observable quantities. If dense hydrate existed within the liquid CO<sub>2</sub> phase, it would be carried by the internal circulation within the CO<sub>2</sub>. It would then be brought towards, and fed into, the floating solid that appeared downstream. We can not exclude that this happens with small units of hydrate carried by the CO<sub>2</sub> phase with only slow sinking. However, such a process can not explain the low density of the solid. If, on the contrary, frazil hydrate is swept along the CO<sub>2</sub>-seawater interface primarily by the stronger water current, it could be entrained into the turbulent water phase and create a mixture of hydrate and seawater. This process would also explain the resulting density which obviously is intermediate between the density of CO<sub>2</sub> and that of seawater. The constraint that the density of the floating solid has to be less than that of liquid CO<sub>2</sub> can be used to give a lower bound on the fraction of seawater of the mixture. With density of seawater 1047 kg m<sup>-3</sup>, of liquid CO<sub>2</sub> 1077 kg m<sup>-3</sup> and of perfect hydrate with all cavities occupied (CO<sub>2</sub> nH<sub>2</sub>O where n=5.75) 1130 kg m<sup>-3</sup>, the solid has to contain a seawater fraction of at least 64%. This is a robust estimate if we assume that the entrained water keeps the same salinity and temperature as the ambient water. If salt is rejected during the process (lowering the density of the water component), or if the hydrate does not have the perfect crystallographic lattice formation (reducing hydrate density), the water fraction could be a few percent smaller. A temperature increase is expected in connection with hydrate formation [8], but would be equilibrated with the seawater over the time scale of the experiment. The solid has observable structure and heterogeneities on the centimetre scale suggesting that it is a mechanical mixture in which macroscopic pockets exist where seawater could keep its salt content. Other experimental protocols and more detailed studies would be required to determine the internal structure. At present we prefer to describe its deviation from perfect hydrate by the fraction of additional seawater, estimated to be between 64 and 100% of the total mass.

If a similar mixture was created in the shallow "upside-down" experiment again by entrainment of frazil hydrate into the turbulent water phase, its density would be higher than that of seawater since pure hydrate is more dense than seawater, so it would sink into seawater before attaining observable size. Thus, the general process of development of a hydrate-seawater mixture at the interface is in agreement with the rapid dissolution observed at the shallower depth. With data from experiments at two depths only, we can not be certain how the floating solid in the deep case is formed nor what controls the mass fractions. We note however, that similar solid was not observed in previous experiments at 3600 m [9] in less dynamically active conditions. Thus, a sufficiently energetic current may be required to entrain hydrate and create such a mixture.

The formation of frazil hydrate and its downstream collection in the deep experiment has similarities to sea ice production by cooling at the ocean surface in high latitudes. Sea ice production is particularly efficient in open-water regions, so-called polynyas or leads, since the low heat conductivity of ice rapidly reduces the freezing rate with increasing ice thickness. The first ice crystals that form at the ocean surface are called frazil. While still unconsolidated, frazil and grease ice are often transported by wind to the edge of the polynya where the ice consolidates and continues to grow as congelation ice. The so-called collection thickness marks the transition between frazil and consolidated ice and is an important but not well observed nor fully understood parameter in models of polynya opening and closure, brine rejection and dense-water formation [10]. Newly formed sea ice is

heterogeneous on the millimetre to centimetre scale and consists of a combination of pure ice crystals plus brine pockets and channels containing high-salinity liquid water. The presently observed transition from a thin layer of "frazil" CO<sub>2</sub>-hydrate seen to move along the interface towards the downstream end under the action of water currents to a consolidated mass when reaching a certain collection thickness, seems reasonably analogous to the sea-ice formation occurring under the action of wind in polynyas. We believe that the mechanically formed, consolidated hydrate mass, because of its buoyancy relative to liquid CO<sub>2</sub>, must also trap liquid water perhaps in macroscopic pockets similar to those in sea ice.

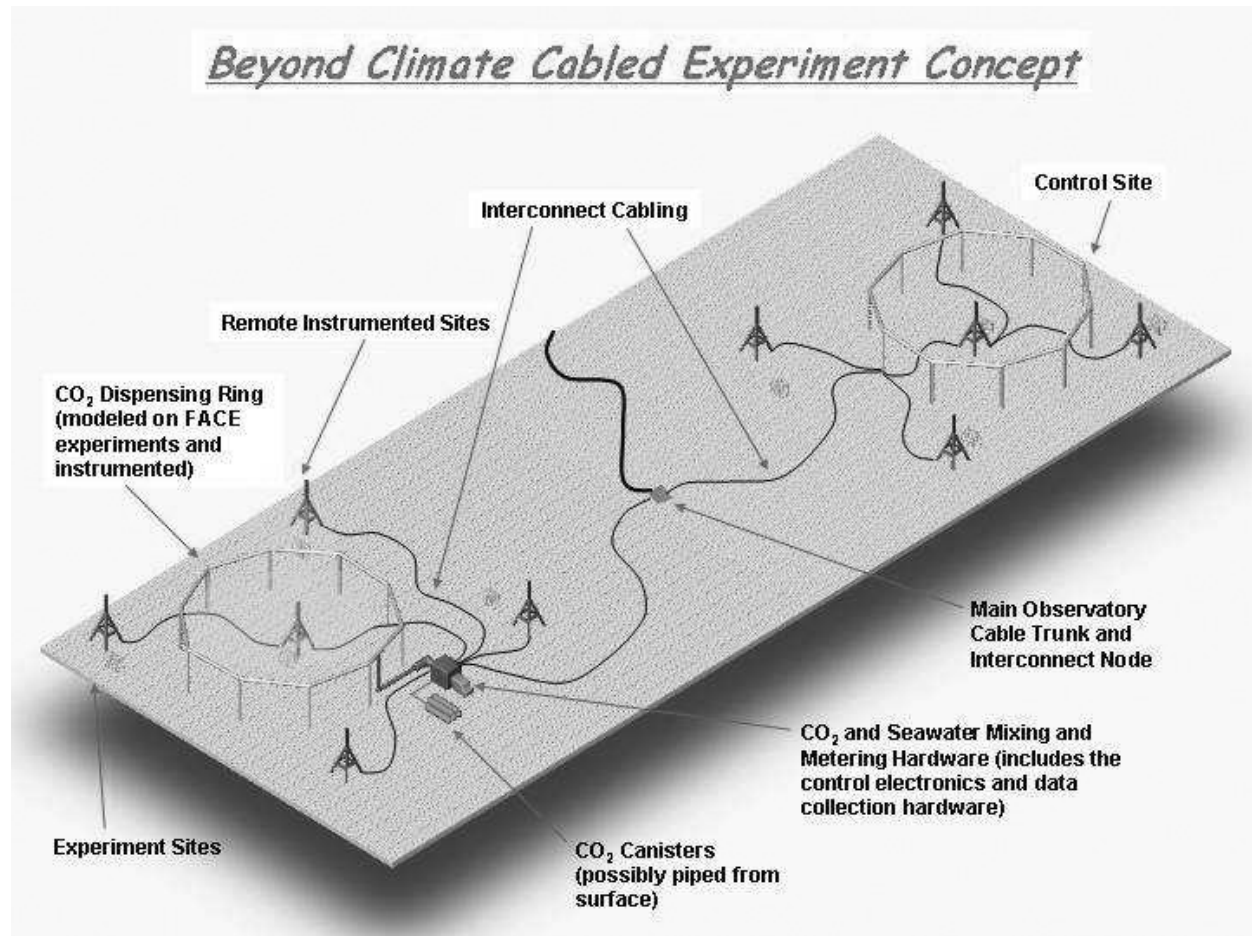
Whether the existence of a thick, consolidated hydrate layer can significantly delay the dissolution of liquid CO<sub>2</sub> stored below could not be observed in the present experiment. [6] recently made detailed *in situ* observations of dissolution of artificially created CO<sub>2</sub> hydrate samples with cylindrical shapes ~2.2 cm in diameter and 3 cm in length at 1028 m depth in water of 3.5°C exposed to naturally varying flow conditions. The samples completely dissolved in four hours, and diameter reduction rates of about 1 μm sec<sup>-1</sup>, corresponding to dissolution rates of about 4 mmolCO<sub>2</sub> m<sup>-2</sup> sec<sup>-1</sup>, are given in [6]. Companion experiments with CH<sub>4</sub> hydrates, and the observed response of CO<sub>2</sub> dissolution rate to time-varying currents, confirmed the assumption of diffusion-controlled dissolution governed by solubility. Since the solubility of CO<sub>2</sub> in seawater in the hydrate regime is lower at 4 km depth than at 1 km depth, dissolution is expected to be slower in our case than in that of [6], but still rapid compared to previously modelled release rates from large-scale storage on the seafloor [11].

Two-fluid models have been developed and applied to situations where buoyant CO<sub>2</sub> droplets are released in the water column [12, 13, 14] addressing the coupled problem of dissolution, plume formation and dynamic effects of dissolved CO<sub>2</sub> *via* seawater density. A similar modelling approach might be envisioned for the case where discrete parcels of CO<sub>2</sub> are torn off from a CO<sub>2</sub> pool and transported downstream. The existing models have been used for fixed initial droplet sizes. In order to be meaningful for the seafloor instability case, some estimate of initial CO<sub>2</sub> parcel-size distribution would be required, presumably obtained from experiments similar to those reported here. Our rough size estimate for these parcels (in the order of 1 cm) compares well with a peak in the energy spectrum of the interface motion at around 0.8 cm found in [4] using wavelet analysis of the intensity variations in the video images. It seems reasonable that the parcel size is linked to this scale associated with interface break-up. In combination with published estimates of shrinkage rates of hydrate covered CO<sub>2</sub> droplets [7, 8, 9], the 1 cm size parcels have a suggested life-span of about one hour. With currents in the 20 to 30 cm sec<sup>-1</sup> range, this translates to advection distances in the order of 1 km until dissolution. This length scale is comparable to the size of potential CO<sub>2</sub> pools for deep-sea storage schemes, implying that shear-driven tear up of the interface and advection of CO<sub>2</sub> parcels might be a significant mechanism for transporting CO<sub>2</sub> away from the storage site in conditions of strong deep-sea currents.

The possibility of actively perturbing the CO<sub>2</sub>-seawater interface by a wave-maker and thruster proved very fruitful in the present experiments and should be continued in the near future, notably in a planned OACE experiment in 2004. In contrast to previous laboratory and field experiments with pure hydrate, the present deep experiments exposed the CO<sub>2</sub> and hydrate to suspended sediments carried by the flowing water (Figures 2 b and c). Intentional storage of larger amounts of CO<sub>2</sub> on the seafloor would also likely be exposed to sediments depending on the current conditions. Both the weight of sediments and their interaction with the hydrate chemistry may affect the development of the CO<sub>2</sub> pool. This is an important topic for further investigation.

Larger scale and longer term experiments are required to further investigate several of the processes studied here, such as dynamical control and scaling effects of collection thickness and the decay of a solid hydrate-seawater mixture. Such experiments require stable power supply, data transmission and remote control over time periods that may exceed normal cruise legs. Since ship schedules may be adversely affected by weather conditions, it is tempting to strive for experimental set-ups that are independent of surface tethering for extended periods, and would only require a ship during deployment and recovery. Designs for multipurpose seafloor cabled observatories with adequate specifications (power in the kW range and signal transmission in the order of 100 Mbit sec<sup>-1</sup>) are now emerging. We suggest that physical, chemical and biological CO<sub>2</sub> experiments could be a prime driver for accelerated development of such initiatives. Biological-impact experiments using pure CO<sub>2</sub> and CO<sub>2</sub>-enriched seawater could be designed based on experience from smaller surface mesocosm experiments in the marine realm, and the so-called Free Air CO<sub>2</sub> Enrichment experiments (FACE, see e.g. <http://www.face.bnl.gov/>) that have been going on in terrestrial systems for several years. The world ocean is already experiencing significantly elevated carbon concentrations due to emissions to the atmosphere and invasion across the air-sea interface [15]. We suggest

that Free Ocean Carbon Enrichment (FOCE) experiments should be considered in a research strategy to address physical, chemical and biological aspects of both direct injection and invasion of CO<sub>2</sub> from the atmosphere.



**Figure 3:** Sketch of possible long-term seafloor experimental set-up with perturbed and control enclosure (figure credit: W. Kirkwood, MBARI).

## CONCLUSIONS

The OACE team has worked successfully together. It has been of tremendous value and inspiration for the entire team to be involved in joint preparation, execution and analysis of results from field experiments conducted from MBARI. The unique experimental results and the great technical and scientific success of both the first and second OACE field experiments have changed the way in which we think of CO<sub>2</sub> placement in the world ocean and how to model it. Specifically we have found that:

1. If exposed to water currents above a critical speed, liquid CO<sub>2</sub> can be torn off and transported as discrete parcels, while the concentration of dissolved CO<sub>2</sub> in water close to the CO<sub>2</sub> pool remains low.
2. At 3940 m depth, frazil-like hydrate formed at the interface and collected downstream into a layer several centimetres in thickness between the liquid CO<sub>2</sub> and seawater. This solid had a density intermediate between the densities of seawater and CO<sub>2</sub> and dissolved slowly, if at all, on the experimental time scale in the order of a day.

These results demonstrate that realistic dynamical perturbations can make the interaction between CO<sub>2</sub> and seawater at the seafloor more complex than hitherto assumed. Processes occur that are not taken into account in any published models. In particular, lateral transport of hydrate-covered CO<sub>2</sub> parcels would inhibit the formation of a stabilizing density gradient in the water above a CO<sub>2</sub> pool, while the massive formation of a relatively low-density solid at the interface could slow down the dissolution from a larger pool of CO<sub>2</sub>.

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## REFERENCES

1. Brewer, P.G., E.T. Peltzer, I. Aya, P.M. Haugan, R. Bellerby, K. Yamane, R. Kojima, P. Walz, and Y. Nakajima, 2004. Small scale field study of an ocean CO<sub>2</sub> plume. *Journal of Oceanography*, in press.
2. Peltzer, E.T., P.G. Brewer, N. Nakayama, P. Walz, I. Aya, R. Kojima, K. Yamane, Y. Nakajima, P.M. Haugan, J. Hove, and T. Johannessen, 2004. Initial results from a 4 km ocean CO<sub>2</sub> release experiment. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, 48 (2).
3. Brewer, P.G., E.T. Peltzer, P. Waltz, I. Aya, K. Yamane, R. Kojima, Y. Nakajima, P.M. Haugan, and T. Johannessen. In press. Deep ocean experiments with fossil fuel carbon dioxide: Creation and sensing of a controlled plume at 4 km depth. *J. Mar. Res.*
4. Hove, J. and P.M. Haugan. In press. Dynamics of a CO<sub>2</sub> – seawater interface in the deep ocean. *J. Mar. Res.*
5. Hove, J., P.M. Haugan, P.G. Brewer, and E.T. Peltzer, 2004. Observations of waves on the CO<sub>2</sub>-seawater interface at 4 km depth in the deep sea. In: *Proceedings of the 7<sup>th</sup> International Conference on Greenhouse Gas Control Technologies*, Vancouver, BC, September 5-9, 2004.
6. Rehder, G., S.H. Kirby, W.B. Durham, L.A. Stern, E.T. Peltzer, J. Pinkston and P.G. Brewer, 2004. Dissolution rates of pure methane hydrate and carbon-dioxide hydrate in undersaturated seawater at 1000-m depth. *Geochimica et Cosmochimica Acta*, Vol. 68, No. 2: 285-292.
7. Brewer, P.G., E.T. Peltzer, G. Friederich, and G. Rehder, 2002. Experimental determination of the fate of rising CO<sub>2</sub> droplets in seawater. *Environ. Sci. Technol.*, Vol. 36: 5441-5446.
8. Aya, I., K. Yamane, and H. Nariai, 1997. Solubility of CO<sub>2</sub> and density of CO<sub>2</sub> hydrate at 30 MPa. *Energy*, Vol. 22: 263-271.
9. Brewer, P.G., G. Friederich, E.T. Peltzer, and M. Orr, Jr., 1999. Direct experiments on the ocean disposal of fossil fuel CO<sub>2</sub>. *Science*, Vol. 284-5416: 943-945.
10. Haarpaintner, J., J.-C. Gascard, and P.M. Haugan, 2001. Ice production and brine formation in Storfjorden. *J. Geoph. Res.*, Vol. 106 (C7): 14001-14013.
11. Fer, I. and P.M. Haugan, 2003. Dissolution from a liquid CO<sub>2</sub> lake disposed in the deep ocean. *Limnol. Oceanogr.*, Vol. 48, No. 2: 872-883.
12. Alendal, G. and H. Drange, 2001. Two-phase, near-field modeling of purposefully released CO<sub>2</sub> in the ocean. *J. Geoph. Res.*, Vol. 106 (C1): 1085-1096.
13. Sato, T., and K. Sato, 2002. Numerical prediction of the dilution process and its biological impacts in CO<sub>2</sub> ocean sequestration. *J. Mar. Sci. Technol.*, Vol. 6: 169-180.
14. Chen, B., Y. Song, M. Nishio, and M. Akai, 2003. Large-eddy simulation of double-plume formation induced by CO<sub>2</sub> dissolution in the ocean. *Tellus*, Vol. 55B: 723-730.
15. Haugan, P.M. and H. Drange, 1996. Effects of CO<sub>2</sub> on the ocean environment. *Energy Convers. Mgmt.*, Vol. 37, No. 6-8: 1019-1022.